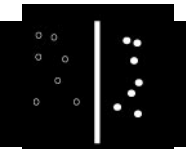
# ION-CONDUCTING MEMBRANES: MEMBRANE SEPARATIONS



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## Introduction

Ceramic membranes are commonly used in separation processes involving the filtration of particulate matter from a fluid stream. This involves the use of controlled porosity ceramic materials, which essentially act as inert filters. More recently, dense ceramic membranes fabricated from ionic conductors have been proposed as active membranes for the high-temperature separation of oxygen from air for a variety of purposes.

The principle of using a dense ceramic ionic conductor to separate the ion-conducting species is, in itself, not new. The idea has been around since the turn of the century when Nernst first investigated solid electrolyte compositions for use as incandescent filaments in his glower devices. Since then ion-conducting ceramics have been used to separate a number of elements, for example oxygen, hydrogen and gallium, but mainly as a scientific curiosity and only on a laboratory scale. The current industrial interest in membrane separators was instigated by a Japanese group, who, in 1985, investigated dense oxide membranes, which were able to permeate substantial fluxes of oxygen at temperatures of 800–1000°C, with 100% selectivity. Since then there has been a rapid growth of both scientific and industrial interest in the use of these membranes for the separation of oxygen. The industrial interest has been driven by the possibility of providing compact oxygen separation plants for a number of applications including aerospace and medical, petrochemical and manufacturing industries.

This article describes a novel oxygen separation process, based on dense ion-conducting ceramic membranes. It is important to note that two different but related devices can be made from such membranes, both of which can be used in the oxygen separation process. In the first device, the driving force is supplied electrically and the membrane is made of an ionic conductor. In the second device, the driving force is supplied by a gradient in oxygen activity and the membrane consists of a mixed ionic electronic conductor. The materials used in the construction of these devices and the devices themselves are described below.

## Materials for Conducting Membranes

Ionic conduction in solids can be achieved in two main ways. Both require crystal structures in which there are a number of equivalent, partially occupied atomic sites. This condition of partial occupancy can occur either by the disordering of a low-temperature structure over two approximately equivalent sublattices, or by promoting large deviations from stoichiometry. Such oxygen ion-conducting materials can be further sub-divided into two groups: *electrolytes* that exhibit predominantly ionic conduction; and *mixed conductors*, materials in which there are both significant electronic and ionic contributions to the total conductivity. A useful concept to introduce at this point is the ionic transference number $t_i$. The ionic transference number is defined as the fractional contribution of the ionic component to the total conductivity. For a mixed conductor with both ionic ($\sigma_i$) and electronic ($\sigma_e$) conductivity, $t_i$ is defined as:

$$t_i = \frac{\sigma_i}{\sigma_i + \sigma_e} \qquad [1]$$

Clearly for solid electrolytes we require $t_i$ to be very close to 1 and for mixed conductors $t_i < 1$.

The ionic conductivity of both types of material is thermally activated. The empirical relationship describing the ionic conductivity is given by:

$$\sigma = \frac{\sigma_0}{T} \exp\left\{\frac{-E_A}{kT}\right\} \qquad [2]$$

where $\sigma_0$ is a constant pre-exponential factor, $T$ is the absolute temperature, $k$ the Boltzmann constant and $E_A$ the observed activation energy for the process. Appreciable ionic conductivity for most oxygen conductors, greater than $10^{-1}\,S\,cm^{-1}$, is only achievable at high temperatures (600–900°C) as the activation energies are always substantial ($\sim$50–100 kJ mol$^{-1}$).

## Solid Electrolytes

Most practical oxide ion conductors are non-stoichiometric and are characterized by their ability

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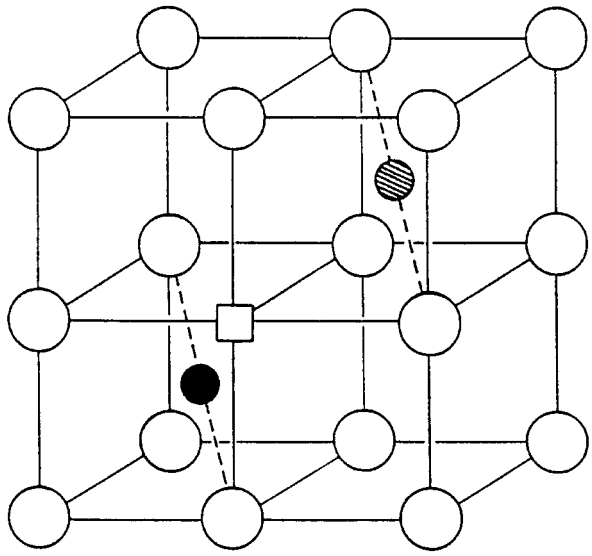

**Figure 1** A half-unit cell of the fluorite structure showing a dopant cation and oxygen vacancy. ○, $O^{2}$-ion; ●, host cation ($4^+$); □, vacancy; ▨, dopant cation ($2^+$ or $3^+$).

to accommodate large departures from the ideal oxygen stoichiometry, without breakdown of the crystal structure. For example, oxides of the fluorite structure shown in **Figure 1** display high ionic conductivities when doped with lower valent cations. In one such material, gadolinia doped ceria, the trivalent gadolinium substitutes for the tetravalent cerium ion, causing a charge imbalance in the lattice. The deficit of positive charge is balanced by the formation of oxygen vacancies, which restores the charge balance (see Figure 1). This process can be formalized into a defect equation using Kröger–Vink notation:

$$Gd_2O_3 \rightarrow 2Gd'_{Ce} + V^{\bullet\bullet}_O + 3O^x_O \qquad [3]$$

Ion transport (and hence charge transport) can take place in such materials by a mechanism involving 'hopping' into neighbouring vacant oxygen sites, provided the ion has sufficient energy to overcome the activation barrier, $E_m$, associated with the ionic migration. High ionic conductivity can be achieved by ensuring an optimum level of doping. Because of the relatively stable nature of the cations used in these materials there is a negligible electronic component to the conductivity, especially at high oxygen pressures.

Of the fluorite oxides, considerable attention has been given to the cubic stabilized zirconia ($ZrO_2$) system for application in both the ceramic oxygen generator (COG) and a closely related device, the solid oxide fuel cell (SOFC). Zirconia with 8 mol% $Y_2O_3$ (8-YSZ) adopts the fluorite structure and is a pure ionic conductor over a wide range of oxygen partial pressures; however, as mentioned above, substantial ionic conductivity is only obtained at temperatures above 900°C. Ceria-gadolinia (CGO) displays similar ionic conductivity to YSZ but at much lower temperatures ($\sim$700°C), principally owing to a lower value of the activation energy observed for the conduction process. The main concern with CGO is that its electronic conductivity becomes substantial under reducing conditions due to the reduction of $Ce^{4+}$ to $Ce^{3+}$, which renders CGO unsuitable for high temperature applications where low partial oxygen pressures occur.

Of increasing interest is a new series of solid solutions which adopt the perovskite structure (see below) based on the parent compound $LaGaO_3$ (lanthanum gallates). Doped gallates of the type $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM) have comparable ionic conductivity to CGO and do not appear to have any appreciable electronic conductivity. **Figure 2** shows a comparison of selected fluorite and perovskite ionic conductors as a function of temperature.

## Mixed Conductors

Most of the mixed conductors of technological interest adopt the perovskite ($ABO_3$) structure (**Figure 3**). The structure is able to accommodate the substitution of many different cations into its framework, assuming the necessary ion size constraints are met. Again, non-stoichiometry is the key to achieving high transport rates of oxygen; however, in these materials, by definition, the electronic component of the conductivity is not negligible. Taking the perovskite-structured material lanthanum cobaltate ($LaCoO_3$) as an example, when a divalent cation such as strontium is substituted for trivalent lanthanum on the A-site, charge compensation takes place by a dual mechanism. This involves the creation of oxygen vacancies and a change in valency of the cobalt from $Co^{3+}$ to $Co^{4+}$. As described earlier, this substitution can be expressed in a defect equation using Kröger–Vink notation of the type:

$$\tfrac{1}{2}O_2 + 4SrO \rightarrow 4Sr'_{La} + V^{\bullet\bullet}_O + 2h^{\bullet} + 5O^x_O \qquad [4]$$

where $h^{\bullet}$ represents an electronic hole ($Co^{4+}$). In this case both electronic compensation and vacancy compensation of the substitutional occurs, and $t_i$ is usually substantially less than one.

One problem associated with the mixed conducting perovskite and perovskite-related materials is that the dual compensation mechanism leads to changing non-stoichiometry with temperature and atmosphere,

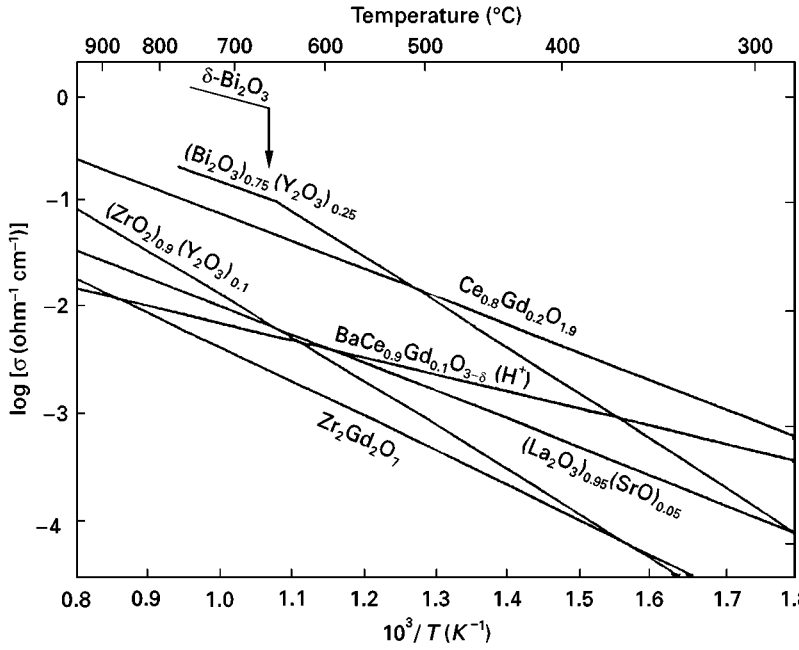


**Figure 2** Oxygen ion conductivity of selected fluorite, fluorite-related and perovskite oxides.

i.e. the balance of vacancy and electronic compensation of the dopant changes with conditions. This manifests itself in a loss or gain of oxygen from the lattice. Most notable is the loss of oxygen with temperature in a constant environment, and/or the sensitivity of the materials to oxygen activity at constant temperature. This loss of oxygen causes a large effective expansion coefficient, which can cause cracking of the membranes upon heating and/or upon the imposition of an oxygen activity gradient.

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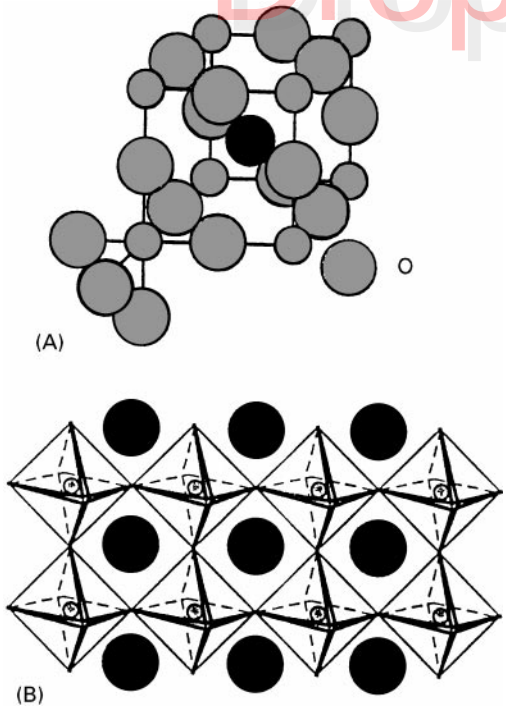


**Figure 3** The perovskite structure. (A) Unit cell and (B) extended structure showing the corner-sharing $BO_6$ octahedra. ●, cation A; ◍, cation B.

## Dual Phase

Finding a single phase ceramic material that has high electronic and ionic conductivity while remaining mechanically and chemically stable is not a trivial matter – in fact, these requirements are often mutually exclusive. Materials that exhibit high oxygen ion fluxes also tend to possess high thermal expansion values, which can lead to catastrophic failure in a membrane subjected to a significant oxygen partial pressure gradient, as mentioned above. A way round this problem is to construct dual-phase membranes, effectively making a mixed conductor on a macroscopic scale (**Figure 4**). Such dual-phase materials consist of two separate phases, one an ionic conductor (e.g. YSZ) and the other an electronic conductor (Ag), which are mixed in suitable proportions to provide connectivity for both phases. The individual components are themselves stable at high temperature and in an oxygen pressure gradient. It is not as yet clear what is the best materials combination, or how to optimize the microstructures in order to maximize the oxygen flux that the membrane can transport.

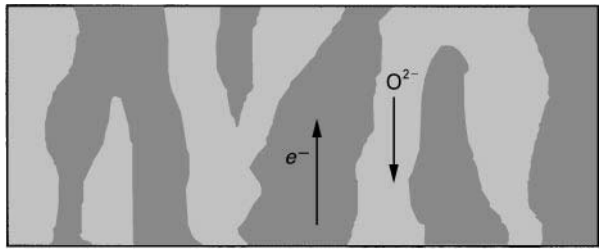


**Figure 4** Schematic of a dual-phase membrane incorporating an ionic and electronic conducting phase.

## Ion-Conducting Membrane Devices

### Pressure Driven Devices

Pressure driven devices are perhaps the simplest form of ceramic oxygen generator. The membrane consists of a dense, gas-tight mixed ionic–electronic conductor (MIEC), which allows the transport of both oxygen ions and electronic species. The driving force for oxygen transport is a differential oxygen chemical potential applied across the membrane. This is achieved by applying a higher partial pressure of oxygen on the membrane feed side than on the permeate side (see **Figure 5**). The whole device may be operated well in excess of atmospheric pressure to achieve a pressurized permeate stream. The most practical design of such a device would be a series of thin-walled tubes. Obviously, the mechanical integrity of such a system is a major concern when very thin membranes are used, and some type of porous support would have to be employed in this case.

The device operates in the following manner. The first step is a surface reaction at the high-pressure surface of the membrane. The gaseous oxygen molecules interact with electrons at 'active' sites on the surface, they dissociate, become ionized and finally are incorporated into the oxide. The rate of this reaction is governed by the gas–solid surface exchange coefficient, $k$. The second step is the diffusion of the oxide ions through the material to the lower pressure side where the reverse process occurs and oxygen is evolved, releasing electrons. The membrane in a pressure-driven device is electrically isolated, that is, there are no external electrical current paths. Thus, the membrane material must be a good electronic conductor to provide a return path for the electrons, providing a compensatory flux of electronic species to balance that of the oxygen ions. Normally, the level of electronic conductivity ($\approx 10^2$–$10^3$ S cm$^{-1}$) in these materials is much higher than the corresponding ionic conductivity ($\approx 1$–$10^{-1}$ S cm$^{-1}$), i.e. $t_i \ll 1$, consequently it is the oxygen transport parameters that determine the achievable oxygen fluxes.

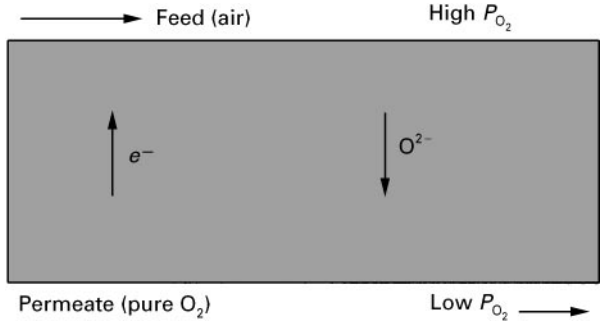


**Figure 5** Schematic of a pressure-driven ceramic oxygen generator based on a mixed conducting oxide.

In this case, a simplifying model can be applied which allows some insight into the operation of the membranes. The ionic current through the membrane can be described in terms of the simple equivalent circuit shown in **Figure 6**. The apparent potential $\eta$ is provided by the partial pressure drop across the membrane, and is defined using the Nernst equation:

$$\eta = \frac{RT}{4F} \ln\left\{\frac{P'_{O_2}}{P''_{O_2}}\right\} \qquad [5]$$

where $P'_{O_2}$ and $P''_{O_2}$ refer to the partial pressure of oxygen on each side of the membrane, $T$ is the temperature, $F$ is Faraday's constant, and $R$ is the gas constant. The membrane resistance (expressed as area specific resistance R.A (ohm cm$^2$)) is then described in terms of two components, the resistance of the bulk of the membrane to the passage of the ionic current $R_0$ and the resistance of the surface of the materials caused by the oxygen exchange process. This latter term is expressed as an equivalent electrode resistance $R_E$, assigned equally to both high and low pressure surfaces. The chief utility of this model is that it allows an easy visualization of the processes involved and it can be applied to the electrically driven separator with a slight modification. The ionic current density, $J_{O^{2-}}$ (A cm$^{-2}$), through the membrane of thickness $L$ and of ionic conductivity $\sigma$ can be expressed as:

$$J_{O^{2-}} = \frac{\eta}{(2R_E + R_0)} \qquad [6]$$

$$= \frac{\eta}{\left(2R_E + \frac{L}{\sigma}\right)} \qquad [7]$$

$R_E$ can be expanded in terms of the surface exchange coefficient for the oxygen exchange process, $k$,

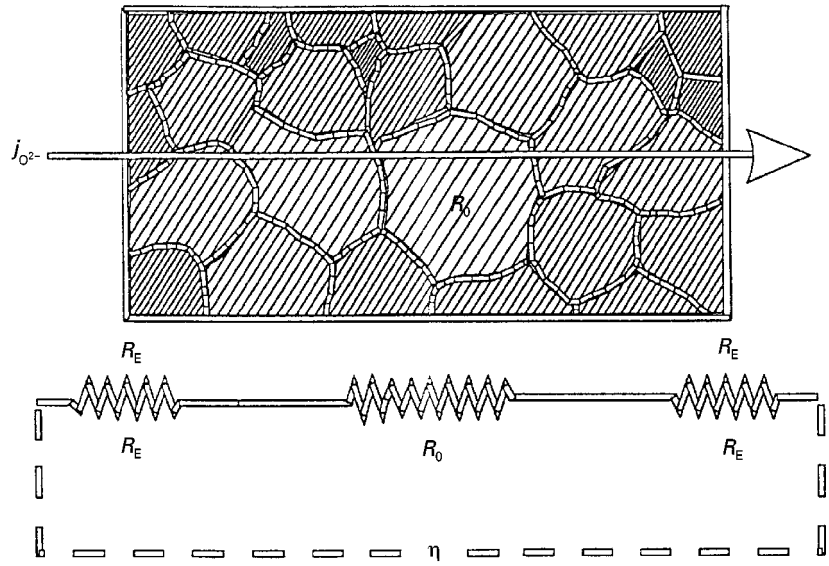


**Figure 6** Equivalent circuit for a ceramic membrane device showing the ionic current.

and the diffusion coefficient, $D$:

$$J_{O^{2-}} = \frac{\eta}{\left\{\frac{2D}{\sigma k} + \frac{L}{\sigma}\right\}} \quad [8]$$

The flux of oxygen through a pressure-driven device can be increased by making the membrane thinner (reducing $R_0$), but this is true only up to a certain point. The surface reaction kinetics ($\equiv R_E$) limit the ultimate flux of oxygen through a thin membrane, and beyond a certain characteristic limiting thickness, $L_c$, the flux remains constant. The numerical value of $L_c$ is given by ratio $D/k$, which for most mixed conducting oxides of interest is approximately 100 μm, meaning that a supported thin film structure is probably required for an optimized permeation flux. A comparison of the oxygen fluxes achieved from a range of materials is discussed later.

### Electrically Driven Devices

The electrically driven device consists of a solid electrolyte membrane with electrodes applied to each side to form a tri-layer structure (**Figure 7**). When an electrical potential is applied to the tri-layer, oxygen is reduced at the cathode, passes through the electrolyte as an $O^{2-}$ ion and is evolved as oxygen at the anode. An external electrical connection allows the transfer of electrons from the anode to the cathode. The simple equivalent circuit used for the pressure-driven membrane is still applicable, however, $R_0$ now becomes the electrolyte ASR and $R_E$ the polarization resistance of the electrodes (assumed to be identical).

The flux of oxygen produced by an electrically driven device is directly proportional to the current passing through the membrane (1 A ≡ 3.5 mL $O_2$ $min^{-1}$), provided the ionic transference number is close to unity. Thus, the flux of oxygen for a given applied potential is governed by the resistance of the membrane (the sum of the electrolyte and electrode polarization resistances) and may be increased by either increasing the potential across the membrane or by reducing the resistance of the membrane. The extent to which the voltage can be increased depends largely on the stability of the electrolyte material. High applied potentials lead to the partial reduction of the electrolyte and the consequent increase in electronic conductivity, leading to a loss of efficiency, for example, in a material such as CGO.

The resistance of the membrane may be reduced by decreasing its thickness. Self-supporting electrolyte

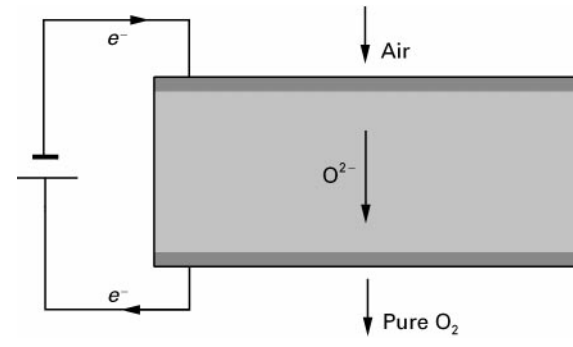


**Figure 7** Schematic of an electrically driven ceramic oxygen generator based on a solid electrolyte. □, Ionic conductor; ■, mixed conductor.

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membranes of the order of 100 μm are available. Thinner electrolytes are not sufficiently strong to support themselves, and therefore further reduction in electrolyte thickness can be achieved by preparing a dense film of the electrolyte on the surface of a porous electrode support. The gains that can be made from switching to thin layers are limited, analogous to the pressure-driven variant. This is because the largest contribution to the resistance of a membrane is usually the polarization resistance of the electrodes, $R_E$, particularly at the lower temperatures of operation. These are independent of the electrolyte thickness ( $\equiv R_0$) and thus again the flux of oxygen is limited by the value of $R_E$.

It is interesting to note that electrode compositions for the electrically driven separator are similar to compositions used as membranes in pressure-driven devices, because the requirements are identical, i.e. a high electronic conductivity and the fast transport of oxygen. Again, the limiting factor turns out to be the kinetics of the surface oxygen exchange reaction at the electrode.

The advantages of electrically driven oxygen separation devices are that large fluxes of oxygen per unit area are possible. At 800°C, an electrical potential of only 0.7 V is equivalent to an oxygen partial pressure gradient ratio of $7 \times 10^{30}$. For applications in which the volume of a device is a key constraint, such as medical and aerospace applications, an electrically driven device would be the favoured option. An added advantage of an electrically driven COG is that the technology is closely related to that of the solid oxide fuel cell (SOFC) currently under development, and appreciable 'spin-off' is expected. The size of the device can be further reduced if a planar geometry is adopted, similar to that of the planar SOFC. Finally, an electrically driven device is also able to produce oxygen at a higher pressure than the air feed-stock, provided the applied potential across the membrane exceeds the back electromotive force due to the partial pressure gradient of oxygen.

The main disadvantage of electrically driven devices is that they are invariably complicated multicomponent devices. This has implications in terms of the thermal and chemical stability, and the compatibility of the various components at the elevated temperature of operation. The need to develop a high-temperature sealant, required for the planar geometry, is an added complication for these compact devices.

## Oxygen Fluxes

Having shown the principle of the devices and having discussed the materials involved, it is of interest to look at the 'state of the art' in terms of the fluxes of oxygen that can be achieved. **Figure 8** shows a range of fluxes

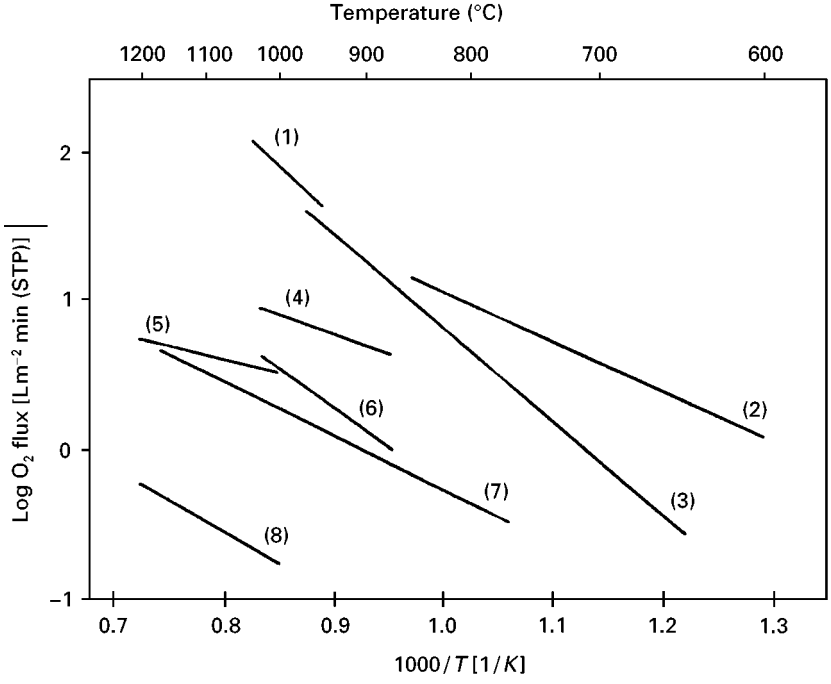


**Figure 8** Arrhenius plots of oxygen permeation for: (1) $SrFeCo_{0.5}O_{3.25-\delta}$; (2) $(Bi_2O_3)_{0.75}$-$(Y_2O_3)_{0.25}$-Ag (35 v/v), 90 μm; (3) $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$; (4) $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$; (5) $La_{0.3}Sr_{0.7}CoO_{3-\delta}$; (6) $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$; (7) $La_{0.5}Sr_{0.5}CoO_{3-\delta}$; (8) YSZ-Pd (40 v/v), continuous Pd-phase.

measured from samples of single and dual-phase materials, operated in a pressure-driven mode, plotted as a function of inverse temperature. This figure is intended to give some appreciation of the fluxes that are attainable; however, they are not normalized to a given partial pressure gradient or thickness of membrane, and thus the fluxes are not directly comparable. Taking a value of between 10 and 100 L $m^{-2}$ $min^{-1}$ as the level of oxygen flux needed for practical applications, it can be seen that the cobalt-containing single-phase materials give appreciable oxygen fluxes above about 900°C. It is interesting to note on this figure that the dual-phase material, fabricated from $(Bi_2O_3)_{0.75}$ $(Y_2O_3)_{0.25}$–Ag (35 v/v), approaches the lower bound of the practical fluxes at temperatures of 800°C.

It is not sensible to put data for electrical driven COGs on the same figure, given the restrictions mentioned above, however, some comparable figures are interesting. An equivalent flux of 15.8 L $m^{-2}$ $min^{-1}$ is readily achievable with planar COG stack based on zirconia and operating at 1000°C. Similar performance has been reported for a system based on a CGO-operating temperature of 800°C.

## Further Reading

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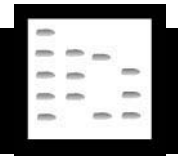
# ION EXCLUSION CHROMATOGRAPHY: LIQUID CHROMATOGRAPHY



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## Introduction

Ion exclusion chromatography (IEC) is a relatively old separation technique, attributed to Wheaton and Bauman, which is now staging an impressive comeback for the simultaneous determination of ionic species. IEC provides a useful technique for the separation of ionic and nonionic substances using an ion exchange stationary phase in which ionic substances are rejected by the resin while nonionic or partially ionized substances are retained and separated by partition between the liquid inside the resin particles and the liquid outside the particles. The ionic substances therefore pass quickly through the column, but nonionic (molecular) or partially ionized substances are held up and are eluted more slowly.

IEC is also referred to by several other names, including ion exclusion partition chromatography, ion chromatography-exclusion mode, and Donnan exclusion chromatography. In this article we use the term ion exclusion chromatography.

Generally, anions (usually anions of weak acids) are separated on a strongly acidic cation exchange resin in the hydrogen form and are eluted as the corresponding fully or partially protonated acids, while cations (usually protonated bases) are separated on a strongly basic anion exchange resin in the hydroxide form and are eluted as the corresponding bases. The eluents used are usually water, water/organic solvent mixtures, dilute (high conductivity) acqueous solutions of a strong acid, or dilute (low conductivity) aqueous solutions of a weak acid. A conductivity detector is commonly used to monitor the column effluent and, when the eluent conductivity is extremely high, a suitable suppressor system is generally used. UV-visible detection is also used as a selective detector in the determination of some aliphatic and aromatic carboxylic acids and some inorganic anions, such as nitrite and hydrogen sulfide. Using IEC, it is posssible to separate weakly ionized anions such as fluoride, phosphate, nitrite, aliphatic carboxylic acids, aromatic carboxylic acids, bicarbonate, borate, aliphatic alcohols, sugars, amino acids, water, and others, as well as ammonium, amines, and others, based on a combination of the separation mechanisms of ion-exlusion, adsorption, and/or size-exclusion. Further discussion of these mechanisms may be found elsewhere in the encyclopedia.